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(54) Porous inorganic material and metal-matrix composite material containing the same and process therefor

Anorganisches poröses Material und dieses enthaltendes Metallmatrixverbundmaterial und Herstellungsverfahren

Matériau inorganique poreux et matériau composite à matrice métallique le contenant et méthode pour sa fabrication

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- PATENT ABSTRACTS OF JAPAN vol. 018, no. 322 (C-1214), 20 June 1994 & JP 06 072800 A (DENKI KAGAKU KOGYO KK), 15 March 1994,

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Description

[0001] This invention relates to a porous inorganic material and a process for producing the same. Particularly, it relates to an in situ synthesized porous inorganic material with a skeleton structure of aluminum borate whiskers useful as a reinforcement of whisker reinforced metal matrix composite materials (WRM), a structural material for high-temperature use, a heat insulating material, a frictional material, a filter medium, and the like, and a process for producing the same. Furthermore, it relates to a metal-matrix composite material comprising a light alloy, such as an aluminum alloy, uniformly reinforced by the in situ synthesized porous inorganic material with a skeleton structure of aluminum borate whiskers and a process for producing the same.

BACKGROUND OF THE INVENTION

[0002] Ceramic whiskers comprising silicon nitride, silicon carbide, alumina, aluminum borate, potassium titanate, titanium oxide, etc. are excellent in mechanical characteristics, heat resistance, corrosion resistance, heat insulating properties, wearability, and electrical insulating properties and have been extending their use in many fields such as WRM, WRP (whisker reinforced plastic), WRC (whisker reinforced ceramic).

[0003] On the other hand, with the recent development of the automobile industry and the aircraft and aerospace industry, there has been an increasing demand for high-strength and high-modulus metallic materials which are light and excellent in heat resistance and wearability. Cases one increasing in which conventional aluminum alloys cannot meet the demand. Reinforcement of metal with heat-resistant fibrous materials or whiskers has been attempted, and many proposals have been made on metallic materials reinforced by this method, i.e., metal-matrix composite materials.

[0004] Whiskers comprising silicon nitride, silicon carbide, alumina, aluminum borate, potassium titanate, titanium oxide, etc. can be exemplified as the typical reinforcements which have hereto been used for production of metal-matrix composite materials. Since it is difficult to disperse extremely fine whiskers in a molten metal uniformly, whisker-reinforced metal-matrix composite materials have generally been obtained by previously forming whiskers into a porous body called a preform and infiltrating a molten metal into the pores of the preform.

[0005] A whisker preform has conventionally been prepared by dispersing whiskers and a binder in water and filtering the aqueous dispersion with suction, followed by drying and calcination. The conventional process has several problems. Firstly, whiskers, which are light and fine, are liable to scatter when dispersed in water and, if inhaled, may endanger workers' health. A strict countermeasure should be taken against scattering. Secondly, while a whisker dispersion is filtered, the whiskers having a needle shape are unavoidably oriented in a specific direction or localized (unevenly distributed), and the orientation and localization remain in the resulting preform. Needless to say, a uniform reinforcing effect cannot be expected from a preform having whiskers oriented or unevenly distributed. Thirdly, since the physical properties of a preform, such as strength and heat resistance, are considerably influenced by the binder used in combination, the excellent properties essential to whiskers cannot be taken full advantage of. Fourthly, it is difficult to obtain a preform having the density and dimensions as originally designed because of considerable change in volume occurring during filtering up to the completion of firing. Another problem is that the whisker preform is extremely expensive because, for one thing, the whiskers as a raw material are expensive.

[0006] The above-mentioned problems have been pointed out with respect to not only a whisker preform itself but various products utilizing a whisker preform, and have made it difficult to take full advantage of the excellent properties of whiskers. Furthermore, when the conventional whisker preform is used for reinforcement of metal, it has following problems. Since the bonding strength among whiskers in a preform is not so strong, the preform tends to be deformed or broken when a molten metal is infiltrated therein. The binder in a preform tends to react with a molten metal, e.g., aluminum, to cause reduction in strength.

[0007] JP-B-6-33193 (the term "JP-B" as used herein means an "examined published Japanese patent publication") discloses a process for producing rigid mullite whisker felt, the process having succeeded in solving the problems associated with preparation of whisker preforms as far as mullite whisker is concerned. The disclosed process comprises heating a green compact comprising a mixture of AlF_3 and SiO_2 in an anhydrous SiF_4 atmosphere at about 700 to 950°C to form rod-like topaz crystals from AlF_3 and SiO_2 , and further heating the topaz crystals at about 1150 to 1700°C to convert to needle-like single crystal mullite whiskers. According to this process, since mullite whiskers are grown by the reaction in a compact, they are bound to each other during the growth, and a whisker felt is completed on the completion of whisker growth. Therefore, filtering process of whiskers to form whisker preform which is accompanied with many difficulties is unnecessary, and the resulting product is therefore free from the above-described drawbacks arising from filtering.

[0008] However, this process, while seeming advantageous, is not easy to carry out because of the involvement of additional cost for the equipment and the process control due to the calcination in a toxic anhydrous SiF_4 atmosphere. Besides, the product is limited to mullite materials, and the applicability of the technique is limited. A process for pro-

ducing whiskers other than mullite whiskers in which whisker formation and formation of a porous body are carried out at the same time is unknown.

[0009] The patent abstract of Japan, volume 18, No. 322 (C-1214) June 20, 1994, mentions JP 06072800, which relates to an aggregate of aluminum borate whiskers and its production. The aggregate is produced by heat-treating a mixture of Al-containing starting material with B-containing starting material, a flux and Sb containing additives. The aggregate with aggregated parts of radially grown acicular crystals consists of acicular crystals grown radially and practically symmetrically in both directions.

[0010] The W090-01471 discloses a process in which AlF_3 and SiO_2 or AlF_3 , SiO_2 and Al_2O_3 powders are formed into a green body of a desired shape and size. The green body is then heated at 700°C to 950°C in an anhydrous SiF_4 atmosphere to form bar-like topaz crystals and then heated in anhydrous SiF_4 atmosphere at about 1150°C to 1700°C to convert the bar-like topaz crystals to needle-like single crystal mullite whiskers which form a porous, rigid felt structure. The felt has the same shape as the green body with about 1.5 or less percent change in linear dimensions. The felt can be used as preforms for ceramic-matrix or metal-matrix composites or by itself as thermal insulation. formation of a porous body are carried out at the same time is unknown.

SUMMARY OF THE INVENTION

[0011] An object of the invention is to provide an in situ synthesized porous inorganic material with a skeleton structure of whiskers, in which the excellent properties essential to whiskers can be fully displayed and to provide a process for producing the porous inorganic material above-mentioned.

[0012] Another object of the invention is to provide a metal-matrix composite material having improved anisotropy and uniformity in its physical properties, being excellent in heat resistance and strength, and being yet inexpensive, as compared with conventional ones prepared by using a whisker preform as a reinforcement.

[0013] A further object of the invention is to provide a process for producing a metal-matrix composite material which is superior in workability and yield to a conventional process using a whisker preform as a reinforcement and provides a product which has improved anisotropy and uniformity in its physical properties and is excellent in heat resistance and strength.

[0014] The above objects are accomplished by the following materials and the following process.

(1) A porous inorganic material (sometimes referred to as "porous ceramic") comprising aluminum borate whiskers distributed uniformly and randomly, in which the individual aluminum borate whisker is bonded to other whisker(s) at one site or more thereof in such a manner that the two or more whiskers share a bond made up of aluminum borate constituting themselves.

(2) A porous inorganic material of item (1), wherein said material is an in situ synthesized porous inorganic material with a skeleton structure of aluminum borate whiskers, which is synthesized by firing of a green (powder) compact of a mixture of aluminum borate whisker-forming raw materials to a skeleton structure of aluminum borate whiskers.

(3) A process for in situ producing a porous inorganic material with a skeleton structure of aluminum borate whiskers comprising uniformly mixing in a powdered state aluminum oxide or an aluminum compound capable of forming aluminum oxide on heating in air, boron oxide or a boron compound capable of forming boron oxide on heating in air, and at least one additive selected from the group consisting of nickel, nickel oxide, vanadium, vanadium oxide, silicon, silicon dioxide, and the compounds capable of forming such oxides on heating in air, compacting the resulting mixed powder in a die, and firing the resulting powder compact to in situ synthesize aluminum borate whiskers.

[0015] In the porous inorganic material of the invention, bonding of the individual whiskers is not by a binder but sharing of aluminum borate constituting each whisker. After an individual aluminum borate whisker comes into contact with other whisker(s) while it is growing, the whisker continues growing while sharing aluminum borate constituting the whiskers at the contact site.

[0016] Therefore, the porous inorganic material has a constitution in which whiskers are bonded at their sides as if they were fused together or two whiskers are crossing each other, one piercing the other. Such a constitution is never observed in the case where previously prepared whiskers are bonded via a binder or by sintering.

[0017] Owing to the fact that the porous inorganic material consists solely of whiskers which are non-oriented and distributed quite randomly and yet uniformly and the fact that a plurality of whiskers are bonded together by sharing a whisker-forming substance without being assisted by a binder, the porous inorganic material of the invention exhibits high strength, high heat resistance and corrosion resistance, in comparison with any conventional whisker preform prepared by using a binder or by sintering.

BRIEF DESCRIPTION OF THE DRAWING

[0018] Figure is a scanning electron micrograph (x2000) of the porous inorganic material obtained in Example 1.

5 DETAILED DESCRIPTION OF THE INVENTION

[0019] The aluminum compound which can be used as a raw material is aluminum oxide or an aluminum compound capable of forming aluminum oxide on heating in air (hereinafter referred to as an aluminum oxide precursor). The aluminum oxide precursor is preferably one capable of forming aluminum oxide on heating at a temperature of about 1000°C or lower in air, with the lower limit of the temperature being generally about 350°C. Examples of the aluminum oxide precursor include aluminum hydroxide, aluminum sulfate, aluminum nitrate, and aluminum chloride.

[0020] The boron compound to be reacted with the aluminum compound is boron oxide (boron trioxide B_2O_3) or a boron compound capable of forming boron oxide on heating in air (hereinafter referred to as a boron oxide precursor). The boron oxide precursor is preferably one capable forming boron oxide on heating at a temperature of about 1000°C or lower, with the lower limit of the temperature being generally about 150°C. Examples of the boron oxide precursor include boric acid (H_3BO_3), tetraboric acid ($H_2B_4O_7$) or metaboric acid (HBO_2).

[0021] In order for the aluminum compound and the boron compound to react at a high temperature to form aluminum borate whiskers, it is necessary to use additive, for example, nickel oxide, metallic nickel powder or a nickel compound capable of forming nickel oxide on heating in air (hereinafter inclusively referred to as a nickel additive). Unless a nickel additive is present, the aluminum compound and the boron compound react only to provide aluminum borate which cannot form whiskers in the case of high Al_2O_3 to B_2O_3 molar ratio (9:2 to 9:6), though it is not clear why the coexistence of the nickel additive enables the formation of aluminum borate whiskers.

[0022] Preferred examples of the nickel compound of forming nickel oxide include nickel hydroxide, nickel chloride, nickel carbonate, and nickel sulfate. The nickel additives may be used either individually or as a combination of two or more thereof.

[0023] The aluminum compound, boron compound and nickel additive are finely powdered and uniformly blended. A preferred mixing ratio is such that on Al_2O_3 to B_2O_3 molar ratio is 9:2 to 9:6, more preferably 9:3 to 9:4.5 and that the amount of the nickel additive is generally from about 0.1 to 10% by weight, preferably about 1 to 2% by weight, based on the total amount of the aluminum compound and the boron compound. At the preferred mixing ratio as specified above, aluminum borate whiskers having a composition of $9Al_2O_3 \cdot 2B_2O_3$ which has particularly excellent heat resistance can be produced at good efficiency. In place of the nickel additive, iron, iron oxide, vanadium, vanadium oxide, silicon, silicon dioxide, and the compounds capable of forming such oxides on heating in air may be used generally in an amount of from 0.1 to 10 % by weight based on the total amount of the aluminum compound and the boron compound.

[0024] The resulting uniform mixture is put in a die and compacted. The shape can be selected arbitrarily according to that of a porous inorganic material to be obtained finally. The higher compacting pressure provides a green compact having a higher density, i.e., a lower porosity. Therefore, by adjusting the compacting pressure, a porous inorganic material having a density falling in the range of from about 0.4 to 1.5 g/cm³, which corresponds to a porosity of about 85 to 50%, can be prepared. If a porous inorganic material having a high porosity exceeding about 85% is desired, it is effective to previously mix the raw materials for molding with carbon black, a powdered organic substance, such as carbon black, synthetic resin powder, starch, etc. The above-described substance can be generally added in an amount of 50 % by weight or less based on the total amount of the aluminum compound and the boron compound. The above-described substance will be burnt away in the subsequent heating step to leave pores thereby reducing the density of the porous inorganic material. By this manipulation, a porous inorganic material having a density minimized to about 0.15 g/cm³ (corresponding to a porosity of about 95%) can be obtained.

[0025] Binders or lubricants for facilitating compacting may be used, while not essential, as far as it does not interfere with whisker growth.

[0026] The green compact removed from the die is then fired in a furnace in air. Where an aluminum oxide precursor and/or a boron oxide precursor is/are used as a raw material, a corresponding oxide is first produced on heating. The firing temperature necessary to produce aluminum borate whiskers from aluminum oxide and boron oxide ranges approximately from 1100 to 1400°C. In this temperature range, boron oxide is considerably vaporized, and the boron oxide partial pressure of the atmosphere increases as a result.

[0027] Upon reaction between aluminum oxide and boron oxide in the presence of nickel additive, aluminum borate crystals, usually having a composition of $9Al_2O_3 \cdot 2B_2O_3$, grow into whiskers. The starting points of growth are distributed uniformly throughout the compact, and the direction of the growth is quite at random in three dimensions. Since the whisker formation proceeds within a dense compact, a growing whisker comes into contact with another growing whisker, whereby aluminum borate is formed at the contact point, which is shared by the two whiskers to provide a bond.

[0028] Even after completion of the reaction for aluminum borate whisker growth, firing may be continued to remove

all the excess boron oxide by vaporization. Alternatively, the excess boron oxide may be washed away with hot water after firing.

[0029] After the reaction, the sintered compact is allowed to cool to provide a porous inorganic material composed of aluminum borate whiskers. The resulting porous inorganic material has substantially the same geometry as the green compact before firing. The shrinkage due to structural change is about 10% at the most. Fine intercommunicating pores remain in the porous inorganic material, and the volume thereof, which is decided by the density of the green compact and the excess of boron oxide, is usually 50 to 95% of the volume of the porous inorganic material. As a result, the porous inorganic material has a density of about 0.15 to 1.5 g/cm³.

[0030] The nickel additive which have participated in whisker formation appears to solubilize in the aluminum borate which constitutes whiskers at a solid state and in the form of an oxide thereof.

[0031] The thus prepared porous inorganic material can be applied to arbitrary uses either as sintered or after cutting. For example, it is useful as a preform for producing WRM or other composite materials, a structural material for high temperature use, a heat insulating material, a filter medium, and the like in the fields where the high heat resistance and excellent corrosion resistance of aluminum boron whiskers and high strength owing to the common bonds made up of the constituting substance can be taken advantage of.

[0032] The metal-matrix composite material of the invention using the thus prepared porous inorganic material as a reinforcement can be obtained by a conventional process, for example, squeeze casting or pressure casting. That is, the porous ceramic body, either as sintered or after appropriate cutting, is preheated sufficiently and set in a die, and a molten matrix metal is infiltrated into the pores under pressure, followed by cooling.

[0033] Suitable examples of the metal which can be used in combination with the porous inorganic material to constitute the composite material include various aluminum alloys and magnesium alloys.

[0034] For WRM, the porous inorganic material prepared by the use of the nickel additive is especially suitable.

[0035] The present invention will now be illustrated in greater detail with reference to Examples, but it should be understood that the invention is not construed as being limited thereto. Unless otherwise indicated, all the parts are by weight.

EXAMPLE 1

[0036] Ten grams of aluminum hydroxide as an aluminum oxide precursor, 3.5 g of orthoboric acid (H₃BO₃) as a boron oxide precursor, and 0.13 g of nickel oxide were thoroughly mixed in a mortar, and the mixed powder was compacted in a die to obtain a green compact having a density of 0.32 g/cm³. The green compact was fired in a furnace at 1250°C for 6 hours to form aluminum borate whiskers. The heating was further continued for an additional 4-hour period at the same temperature to vaporize residual boron oxide, followed by allowing to cool to obtain a porous inorganic material weighing 7.66 g and having a density of 0.47 g/cm³ and a compressive strength of 70 kgf/cm². The aluminum borate whiskers constituting the material was found to have an average diameter of 0.6 μm and a length of 20 to 30 μm. The scanning electron microscope photograph (x2000) of the resulting porous material is shown in Figure.

EXAMPLE 2

[0037] Ten grams of aluminum hydroxide as an aluminum oxide precursor, 3.5 g of orthoboric acid (H₃BO₃) as a boron oxide precursor, and 0.13 g of nickel oxide were thoroughly mixed in a mortar, and the mixed powder was compacted in a die to obtain a green compact having a density of 0.45 g/cm³. The green compact was fired in a furnace at 1250°C for 10 hours to form aluminum borate whiskers, followed by allowing to cool to obtain a porous inorganic material weighing 7.66 g and having a density of 0.71 g/cm³ and a compressive strength of 105 kgf/cm². The aluminum borate whiskers constituting the material was found to have an average diameter of 0.6 μm and a length of 20 to 30 μm.

EXAMPLE 3

[0038] Ten grams of aluminum hydroxide as an aluminum oxide precursor, 2.19 g of orthoboric acid (H₃BO₃) as a boron oxide precursor, and 0.1 g of nickel oxide were thoroughly mixed in a mortar, and the mixed powder was compacted in a die to obtain a green compact having a density of 0.65 g/cm³. The green compact was fired in a furnace at 1300°C for 6 hours to form aluminum borate whiskers. The firing was further continued for an additional 4-hour period at 1250°C to vaporize residual boron oxide, followed by allowing to cool to obtain a porous inorganic material weighing 7.63 g and having a density of 0.94 g/cm³ and a compressive strength of 150 kgf/cm². The aluminum borate whiskers constituting the material was found to have an average diameter of 0.8 μm and a length of 10 to 20 μm.

EXAMPLE 4

[0039] Twenty-two grams of aluminum sulfate as an aluminum oxide precursor, 1.97 g of boron oxide as a boron oxide precursor, and 0.13 g of nickel oxide were thoroughly mixed in a mortar, and the mixed powder was compacted in a die to obtain a green compact having a density of 0.35 g/cm³. The green compact was fired in a furnace at 1200°C for 6 hours to form aluminum borate whiskers. The fired body was washed with hot water to remove residual boron oxide, followed by heat drying, to obtain a porous inorganic material weighing 7.68 g and having a density of 0.43 g/cm³ and a compressive strength of 65 kgf/cm². The aluminum borate whiskers constituting the material was found to have an average diameter of 0.4 μm and a length of 10 to 25 μm.

EXAMPLES 4A to 4C

[0040] Porous inorganic materials were prepared in the similar manner except that the following raw materials were used and synthesis was conducted at 1400°C for 6 hours.

Raw Material 1	
Aluminum hydroxide	70.5 wt%
Boric acid	27.9 wt%
SiO ₂	0.7 wt%
Fe	0.9 wt%

[0041] The obtained porous inorganic material had a density of 0.48 g/cm³ and a compressive strength of 82 kgf/cm².

Raw Material 2	
Aluminum hydroxide	68.9 wt%
Boric acid	27.3 wt%
SiO ₂	0.7 wt%
Fe	0.9 wt%
V ₂ O ₅	2.2 wt%

[0042] The obtained porous inorganic material had a density of 0.50 g/cm³ and a compressive strength of 92 kgf/cm².

Raw Material 3	
Aluminum hydroxide	69.5 wt%
Boric acid	27.3 wt%
SiO ₂	0.7 wt%
Fe ₂ O ₃	2.3 wt%

[0043] The obtained porous inorganic material had a density of 0.48 g/cm³ and a compressive strength of 85 kgf/cm².

[0044] In the porous inorganic material prepared by the use of Fe, Fe₂O₃, SiO₂, and/or V₂O₅ as the additive, the residual amount of the additive in the material is large (5 to 10 wt%), the length of the prepared whiskers is short (about 10 μm to 20 μm), and the diameter thereof is about 0.8 μm. On the other hand, in the porous inorganic material prepared by the use of the nickel compound, the residual amount of the additive in the material is 1 to 2 wt% and the length of the whiskers is 10 to 30 μm. Furthermore, in the case where the porous inorganic material is prepared by the use of Fe, Fe₂O₃, SiO₂, and/or V₂O₅, high temperature is required for preparing the porous inorganic material.

EXAMPLES 5 TO 7

[0045] 73.2 wt% of aluminum hydroxide as an aluminum oxide precursor, 25.8 wt% of orthoboric acid (H₃BO₃) as a boron oxide precursor, and 1 wt% of nickel oxide were thoroughly ground and mixed in a grinding machine. The resulting mixed powder was compacted in a die to obtain three disks having a green density varying from 0.41 to 0.92 g/cm³. The die used had such a shape that a disk-like ceramic having a diameter of 100 mm and a thickness of 20 mm was obtained after firing. The disks were fired in a furnace at 1250°C for 6 hours to in situ synthesize aluminum borate whiskers (9Al₂O₃·2B₂O₃) in the compact. After cooling, the sintered compact was washed with hot water to remove

unreacted boron oxide. Thus, three porous ceramic bodies having a porosity of 80%, 70% or 60% were obtained.

[0046] Composite materials were prepared as follows by using the resulting porous ceramic bodies as a reinforcement and an aluminum alloy as a matrix metal.

[0047] The porous ceramic was preheated to 800°C and placed in a die set at 300°C. A molten aluminum alloy JIS AC8A (JIS H 5202) was pressed into the pores of the porous ceramic under a pressure of 100 MPa and cooled to solidify. The resulting composite material was removed from the die and subjected to a T6 treatment (defined in JIS H 5202).

[0048] A dumbbell specimen having a diameter of 6 mm and a length (parallel portion) of 25 mm was cut out of the composite material to determine tensile strength. A specimen was cut out along the horizontal direction or the pressing direction (perpendicular to the surface of the disk) to determine the coefficient of thermal expansion. The results obtained are shown in Table 1 below. For reference, the measured values of the aluminum alloy used as a matrix (AC8A) are also shown.

EXAMPLES 8 AND 9

[0049] 73.2 wt% of aluminum hydroxide, 25.8 wt% of orthoboric acid (H_3BO_3), and 1 wt% of nickel oxide were thoroughly ground and mixed in a grinding machine. 20 wt% of carbon black was further added to the mixture and mixed uniformly. The resulting mixed powder was compacted in the same die as used in Example 5 to obtain a disk having a density of 0.40 g/cm³ or 0.35 g/cm³. The disks were fired in a furnace at 1250°C for 6 hours to in situ synthesize aluminum borate whiskers ($9Al_2O_3 \cdot 2B_2O_3$) in the compact while burning off carbon black. After cooling, the sintered compact was washed with hot water to remove unreacted boron oxide to give a porous ceramic material having a porosity of 85% or 90%.

[0050] Composite materials were prepared by using the resulting porous ceramic materials as a reinforcement and an aluminum alloy as a matrix metal in the same manner as in Example 5. The physical properties of the resulting material as measured in the same manner as in Example 5 are shown in Table 1.

COMPARATIVE EXAMPLES 1 AND 2

[0051] Commercially available aluminum borate whiskers ($9Al_2O_3 \cdot 2B_2O_3$) were dispersed in 10-fold (by weight) water. To the dispersion was added silica sol in an amount of 2% by weight in terms of SiO_2 based on the whiskers and mixed. The resulting slurry was poured in a cylindrical die for filtration, filtered, and squeezed from the top to obtain a disk. The disk was taken out of the die, dried, and calcined at 1200°C for 1 hour to prepare an aluminum borate whisker preform having a diameter of 100 mm and a thickness of 20 mm. Thus, preforms having a porosity of 70% or 80% were prepared depending on the pressure on squeezing.

[0052] A whisker-reinforced metal matrix composite material was prepared in the same manner as in Example 5, except for using the above prepared whisker preform. The physical properties of the composite material were measured in the same manner as in Example 5. The obtained results are shown in Table 1.

TABLE 1

Example No.	Porosity of Porous Ceramic (%)	Strength (MPa)		Thermal Expansion Coefficient ($\times 10^{-6}$)	
		Room Temp.	350°C	Horizontal Direction	Pressing Direction
Example 5	60	387	191	10.5	10.6
Example 6	70	353	167	12.5	12.4
Example 7	80	315	140	16.1	16.1
Example 8	85	304	116	17.5	17.2
Example 9	90	282	94	19.2	19.4
Comparative Example 1	70	338	140	10.8	15.2
Comparative Example 2	80	283	105	12.9	17.9
Reference (Al Alloy)	-	245	46	20.7	20.9

[0053] As can be seen from Table 1, with the volume percentage of the reinforcement to matrix being equal, the metal-matrix composite materials according to the invention exhibit higher strength at 350°C than those using a conventional preform as a reinforcement. This seems to be because of the higher strength and higher heat resistance

possessed by the porous ceramic material per se than those of the preform. Further, the comparative materials show a marked variation of thermal expansion coefficient depending on the direction, while such a directional difference does not occur in the materials of the invention, proving that the reinforcement used in the invention has perfect isotropy.

[0054] On observing the outer appearance and the cut area of the composite materials, no deformation nor breakage of the reinforcement was found in the materials of Examples, whereas the preform of the comparative composite materials was found suffering deformation and breakage due to casting pressure.

[0055] As has been described and demonstrated, the present invention provides a porous inorganic material composed of aluminum borate whiskers through a simple process comprising compacting a mixture of inexpensive raw materials and firing the green compact to cause reaction. There is no need of using expensive whiskers, which has been prepared by a conventional process to form a whisker preform by filtration. All the problems associated with a conventional process which arise from scattering of whiskers and uneven distribution or orientation of whiskers are solved. Since the product density can be controlled simply by adjusting the compact pressure in mixed powder, it is easy to change the product density in accordance with the end use, and the possible range of the density which the product can have is broader than in a conventional process. The performance of aluminum borate whiskers can be taken advantage of to a possible highest degree in the porous structure in which the whiskers are not oriented in a specific direction and are united into one body via common bonds made up of aluminum borate without relying on a binder. Hence, the porous material is excellent in strength, heat resistance, corrosion resistance as well as uniformity of these characteristics.

[0056] The porous inorganic material used as a reinforcement in the invention composed solely of aluminum borate whiskers which are distributed quite randomly and yet uniformly without being oriented in a specific direction. The bonds connecting the whiskers are strong and chemically stable bonds formed by the individual whiskers' sharing aluminum borate which constitutes themselves without relying on a binder. Therefore, the porous ceramic body can achieve isotropic reinforcement while retaining its original shape without undergoing deformation or breakage under a strong stress imposed during casting. The porous ceramic body shows satisfactory permeability to a molten metal and undergoes no reaction with an infiltrating molten metal.

[0057] The process for producing a whisker reinforced metal-matrix composite material according to the invention is characterized in that a high quality product can be obtained with more excellent workability and in a higher yield than a conventional process using a whisker preform as a reinforcement. Since the in situ synthesized porous ceramic with a skeleton structure of aluminum borate whiskers according to the invention as a reinforcement can have its pore controlled easier and over a broader range than the conventional whisker preform, the ratio of reinforcement to matrix can be varied widely according to the end use.

[0058] While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A porous inorganic material comprising aluminum borate whiskers distributed uniformly and randomly, in which an individual aluminum borate whisker is bonded to other whisker(s) at one site or more thereof in such a manner that the two or more whiskers share a bond made up of aluminum borate constituting the whiskers themselves.
2. The porous inorganic material of claim 1, wherein said material is an in situ synthesized porous inorganic material with a skeleton structure of aluminum borate whiskers, which is synthesized by firing of a green powder compact of a mixture of aluminum borate whisker-forming raw materials to a skeleton structure of aluminum borate whiskers.
3. The porous inorganic material of claim 1, wherein said material has a density of 0.15 to 1.5 g/cm³.
4. The porous inorganic material of claim 1, wherein said aluminum borate whisker has a composition of $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$.
5. A process for in situ producing a porous inorganic material with a skeleton structure of aluminum borate whiskers comprising uniformly mixing in a powdered state aluminum oxide or an aluminum compound capable of forming aluminum oxide on heating in air, boron oxide or a boron compound capable of forming boron oxide on heating in air, and at least one additive selected from the group consisting of nickel, nickel oxide, vanadium, vanadium oxide, silicon, silicon dioxide, and the compounds capable of forming such oxides on heating in air, compacting the resulting mixed powder in a die, and firing the resulting powder compact to in situ synthesize aluminum borate whiskers.

6. The process of claim 5, wherein the additive is at least one selected from nickel oxide, nickel, and a nickel compound capable of forming nickel oxide on heating in air.
7. The process of claim 5, wherein said aluminum oxide or said aluminum compound capable of forming aluminum oxide and said boron oxide or said boron compound capable of forming boron oxide are used at a molar ratio of 9:2 to 9:6, in terms of Al_2O_3 to B_2O_3 .
8. The process of claim 5, further comprises, after formation of the aluminum borate whiskers, removing excess of said boron oxide by heating at a high temperature or washing with hot water.
9. The process of claim 6, wherein said nickel oxide, said nickel or said nickel compound capable of forming nickel oxide is used in an amount of 0.1 to 10% by weight, in terms of nickel oxide, based on the total amount of said aluminum oxide or said aluminum compound capable of forming aluminum oxide and said boron oxide or said boron compound capable of forming boron oxide.
10. The process of claim 6, wherein said firing is at 1100 to 1400°C.
11. The process of claim 6, further comprises, after formation of the aluminum borate whiskers, removing excess of said boron oxide by heating at a high temperature or washing with hot water.
12. A porous ceramic-reinforced metal-matrix composite material uniformly reinforced with a porous inorganic material as defined in claim 1, which is obtained by firing a green compact of a mixture of aluminum borate whisker-forming raw materials to in situ synthesize aluminum borate whiskers in said compact.
13. The porous ceramic-reinforced metal-matrix composite material of claim 12, wherein said aluminum borate whisker has a composition of $9Al_2O_3 \cdot 2B_2O_3$.
14. A process for producing a porous ceramic-reinforced metal-matrix composite material, the process comprising a process as defined in claim 5 for preparing a porous ceramic body, preheating the resulting porous ceramic body, pressing a molten matrix metal into the pores of the porous ceramic material, and cooling the infiltrated ceramic body to solidify said metal.
15. The process of claim 14, wherein said aluminum borate whiskers have a composition of $9Al_2O_3 \cdot 2B_2O_3$.

Patentansprüche

1. Poröses, anorganisches Material, das Aluminiumborat-Whisker aufweist, die gleichförmig und zufällig verteilt sind, wobei ein individueller Aluminiumborat-Whisker an einen anderen Whisker (andere Whisker) an einer Stelle oder mehreren davon in einer solchen Art und Weise gebunden ist, daß die zwei oder mehr Whisker eine Bindung gemeinsam teilen, die aus Aluminiumborat aufgebaut ist, das die Whisker selbst bildet.
2. Poröses, anorganisches Material nach Anspruch 1, wobei das Material ein in situ synthetisiertes, poröses, anorganisches Material mit einer Skelettstruktur aus Aluminiumborat-Whiskern ist, das durch Brennen eines Pulvergrünlings einer Mischung aus Aluminiumborat-Whisker bildenden Ausgangsmaterialien zu einer Skelettstruktur aus Aluminiumborat-Whiskern synthetisiert ist.
3. Poröses, anorganisches Material nach Anspruch 1, wobei das Material eine Dichte von 0,15 bis 1,5 g/cm³ besitzt.
4. Poröses, anorganisches Material nach Anspruch 1, wobei der Aluminiumborat-Whisker eine Zusammensetzung von $9Al_2O_3 \cdot 2B_2O_3$ besitzt.
5. Verfahren zum Herstellen in situ eines porösen, anorganischen Materials mit einer Skelettstruktur aus Aluminiumborat-Whiskern, umfassend das gleichförmige Mischen in einem pulverförmigen Zustand von Aluminiumoxid oder einer Aluminiumverbindung, geeignet zum Bilden von Aluminiumoxid beim Erwärmen in Luft, Boroxid oder eine Borverbindung, geeignet zum Bilden von Boroxid beim Erwärmen in Luft, und mindestens einem Additiv, ausgewählt aus der Gruppe, die besteht aus Nickel, Nickeloxid, Vanadium, Vanadiumoxid, Silizium, Siliziumdioxid, und den Verbindungen, die zum Bilden solcher Oxide beim Erwärmen in Luft geeignet sind, Kompaktieren des erhal-

tenen, gemischten Pulvers in einer Form und Brennen des erhaltenen Pulverpreßlings, um in situ Aluminiumborat-Whisker zu synthetisieren.

- 5 6. Verfahren nach Anspruch 5, wobei das Additiv mindestens eines ist, ausgewählt aus Nickeloxid, Nickel, und einer Nickelverbindung, geeignet zum Bilden von Nickeloxid beim Erwärmen in Luft.
7. Verfahren nach Anspruch 5, wobei das Aluminiumoxid oder die Aluminiumverbindung, geeignet zum Bilden von Aluminiumoxid, und das Boroxid oder die Borverbindung, geeignet zum Bilden von Boroxid, in einem Mol-Verhältnis von 9:2 bis 9:6, im Hinblick auf Al_2O_3 zu B_2O_3 , verwendet werden.
- 10 8. Verfahren nach Anspruch 5, das weiterhin, nach der Bildung der Aluminiumborat-Whisker, ein Entfernen eines Überschusses des Boroxids durch Erwärmen bei einer hohen Temperatur oder durch Spülen mit heißem Wasser aufweist.
- 15 9. Verfahren nach Anspruch 6, wobei das Nickeloxid, das Nickel oder die Nickelverbindung, geeignet zum Bilden von Nickeloxid, in einer Menge von 0,1 bis 10% bezogen auf das Gewicht, im Hinblick auf Nickeloxid, basierend auf der gesamten Menge des Aluminiumoxids oder der Aluminiumverbindung, geeignet zum Bilden von Aluminiumoxid, und des Boroxids oder der Borverbindung, geeignet zum Bilden von Boroxid, verwendet wird.
- 20 10. Verfahren nach Anspruch 6, wobei das Brennen bei 1100 bis 1400°C erfolgt.
11. Verfahren nach Anspruch 6, das weiterhin, nach der Bildung der Aluminiumborat-Whisker, ein Entfernen eines Überschusses des Boroxids unter Erwärmen bei einer hohen Temperatur oder Spülen mit heißem Wasser, aufweist.
- 25 12. Poröses, mit Keramik verstärktes Metallmatrix-Verbundmaterial, gleichförmig verstärkt mit einem porösen, anorganischen Material, wie es in Anspruch 1 definiert ist, das durch Brennen eines grünen Preßlings aus einer Mischung Aluminiumborat-Whisker bildender Ausgangsmaterialien, um in situ Aluminiumborat-Whisker in dem Preßling zu synthetisieren, erhalten ist.
- 30 13. Poröses, mit Keramik verstärktes Metallmatrix-Verbundmaterial nach Anspruch 12, wobei der Aluminiumborat-Whisker eine Zusammensetzung von $9Al_2O_3 \cdot 2B_2O_3$ besitzt.
14. Verfahren zum Herstellen eines porösen, mit Keramik verstärkten Metallmatrix-Verbundmaterials, wobei das Verfahren ein Verfahren aufweist, wie es in Anspruch 5 definiert ist, zum Präparieren eines porösen Keramikkörpers, vor Erwärmen des erhaltenen, porösen Keramikkörpers, Pressen eines geschmolzenen Matrixmetalls in die Poren des porösen Keramikmaterials hinein und Kühlen des infiltrierten Keramikkörpers, um das Metall zu verfestigen.
- 35 15. Verfahren nach Anspruch 14, wobei die Aluminiumborat-Whisker eine Zusammensetzung von $9Al_2O_3 \cdot 2B_2O_3$ besitzen.
- 40

Revendications

- 45 1. Matériau inorganique poreux comprenant des barbes de borate d'aluminium distribuées uniformément et de manière aléatoire, dans lequel une barbe de borate d'aluminium individuelle est liée à une ou plusieurs autres barbes à un site de celles-ci ou plus, de manière que deux barbes ou plus partagent une liaison formée de borate d'aluminium constituant les barbes elles-mêmes.
- 50 2. Matériau inorganique poreux selon la revendication 1, caractérisé en ce que ledit matériau est un matériau inorganique poreux synthétisé in situ avec une structure de squelette de barbes de borate d'aluminium, qui est synthétisé par chauffage d'un produit pulvérulent compacté non fini d'un mélange de matières premières formant des barbes de borate d'aluminium en une structure de squelette de barbes de borate d'aluminium.
- 55 3. Matériau inorganique poreux selon la revendication 1, caractérisé en ce que ledit matériau a une densité de 0,15 à 1,5 g/cm³.
4. Matériau inorganique poreux selon la revendication 1, caractérisé en ce que ladite barbe de borate d'aluminium

a une composition de $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$.

5. Procédé de préparation in situ d'un matériau inorganique poreux avec une structure de squelette de barbes de borate d'aluminium comprenant le mélange de manière uniforme dans un état pulvérulent d'oxyde d'aluminium ou d'un composé d'aluminium capable de former de l'oxyde d'aluminium par chauffage dans l'air, d'oxyde de bore ou d'un composé de bore capable de former de l'oxyde de bore par chauffage dans l'air, et d'au moins un additif choisi dans le groupe constitué par le nickel, l'oxyde de nickel, le vanadium, l'oxyde de vanadium, le silicium, le dioxyde de silicium, et les composés capables de former ces oxydes par chauffage dans l'air, le compactage de la poudre mixte résultante dans un moule, et le chauffage du produit compacté de poudre résultant pour synthétiser in situ des barbes de borate d'aluminium.
6. Procédé selon la revendication 5, caractérisé en ce que l'additif est au moins un choisi parmi l'oxyde de nickel, le nickel, et un composé de nickel capable de former l'oxyde de nickel par chauffage dans l'air.
7. Procédé selon la revendication 5, caractérisé en ce que ledit oxyde d'aluminium ou ledit composé d'aluminium capable de former l'oxyde d'aluminium et ledit oxyde de bore ou ledit composé de bore capable de former l'oxyde de bore sont utilisés en un rapport molaire de 9 : 2 à 9 : 6, en termes de Al_2O_3 à B_2O_3 .
8. Procédé selon la revendication 5, comprenant en outre, après la formation des barbes de borate d'aluminium, l'élimination de l'excès dudit oxyde de bore par chauffage à une température élevée ou lavage avec de l'eau chaude.
9. Procédé selon la revendication 6, caractérisé en ce que ledit oxyde de nickel, ledit nickel ou ledit composé de nickel capable de former l'oxyde de nickel est utilisé en une quantité de 0,1 à 10% en poids, en termes d'oxyde de nickel, rapportée à la quantité totale dudit oxyde d'aluminium, ou dudit composé d'aluminium capable de former l'oxyde d'aluminium et dudit oxyde de bore ou dudit composé de bore capable de former l'oxyde de bore.
10. Procédé selon la revendication 6, caractérisé en ce que ledit chauffage est à 1100 à 1400°C.
11. Procédé selon la revendication 6, qui comprend en outre, après la formation des barbes de borate d'aluminium, l'élimination d'excès dudit oxyde de bore par chauffage à une température élevée ou lavage à l'eau chaude.
12. Matériau composite à matrice métallique renforcée par une céramique poreuse renforcé uniformément par un matériau inorganique poreux tel que défini dans la revendication 1, qui est obtenu par chauffage d'un produit compacté non fini d'un mélange de matières premières formant des barbes de borate d'aluminium pour synthétiser in situ des barbes de borate d'aluminium dans ledit produit compacté.
13. Matériau composite à matrice métallique renforcée par une céramique poreuse selon la revendication 12, caractérisé en ce que ladite barbe de borate d'aluminium a une composition de $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$.
14. Procédé de préparation d'un matériau composite à matrice métallique renforcée par une céramique poreuse, le procédé comprenant un procédé tel que défini dans la revendication 5 pour préparer un corps céramique poreux, le préchauffage du corps céramique poreux résultant, la compression d'un métal de matrice fondu dans les pores du matériau céramique poreux, et le refroidissement du corps céramique infiltré pour solidifier ledit métal.
15. Procédé selon la revendication 14, caractérisé en ce que lesdites barbes de borate d'aluminium ont une composition de $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$.

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Figure

